

Anodic Gel Polymerization of Acrylic Acid

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ABSTRACT

Electro-initiated polymerization of acrylic acid at room temperature ($\sim 25^{\circ}\text{C}$) was examined by using sodium nitrate as a supporting electrolyte in aqueous medium. When the electric current was passed in reaction mixture then cross-linked water-insoluble gel formation take place in electrolytic cell, about which we report here briefly.

Keywords: Acrylic acid (AA), electro-initiated, sodium Nitrate, aqueous, anodic.

INTRODUCTION

It was observed from literature that the electrolysis of acrylamide in a solution of sodium nitrate in N, N-dimethylformamide leads to polymer formation simultaneously in both the anodic and cathodic compartments¹. The polymerization in the cathode compartment involved an anionic mechanism similar to the alkaline lactum polymerization via amide anions formed by hydrogen transfer according to Breslow *et. al.*² The anodic polymerization was initiated by the species generated by decomposition of the salt at the anode.

This work has been extended to an aqueous system with another vinyl monomer, acrylic acid, in which gel formation take place.

EXPERIMENTAL PART

Materials: Water was fractionally distilled several times. Acrylic acid, sodium

nitrate and other chemicals were of reagent grade and used without further purification.

Polymerization: Polymerization was carried out under ordinary laboratory conditions in a single electrolytic cell using electrodes e.g. stainless steel - stainless steel of the area 0.7 x 2.5 cm. Acrylic acid in H_2O with sodium nitrate as supporting electrolyte forms polymers in electrolytic cell. No polymerization occurred unless the solution was subjected to electrolysis. This showed complete absence of in adventitious initiators and also that electric current was necessary.

RESULTS AND DISCUSSION

On electrolysis, the electrolytic solution, after showing some induction period started to become viscous and transformed from a viscous mixture to a transparent elastic gel, which is perhaps not reversible.

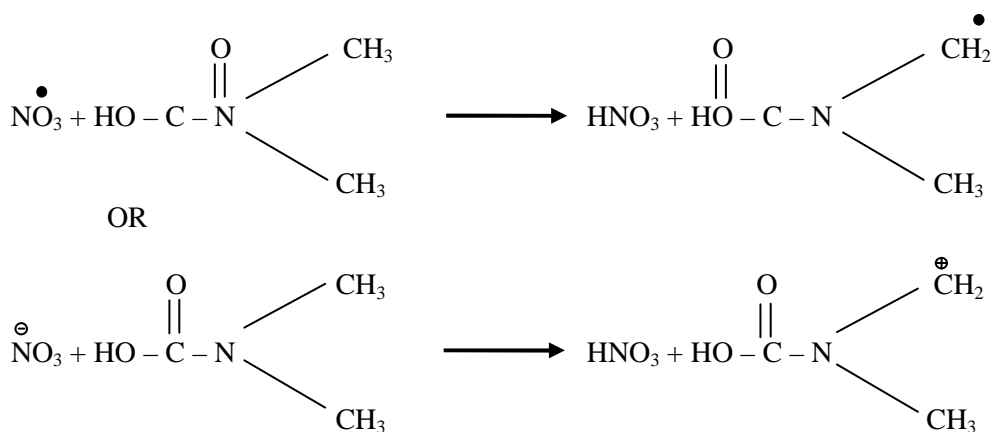
Considerable difficulty was usually encountered in extracting the polymer because it stuck as one solid insoluble block in the electrolytic cell. On drying, the rubber-like gel polymer became hard and brittle, it had glassy appearance.

The incidence of gelation (possibly in finite network formation) was generally observed as the extent of conversion advanced beyond 40%. This point may be attained by increasing either the current level or time of electrolysis (Table-I, Table-II). The gel formation becomes possible only for a fairly

concentrated monomer solution (Table-III). An increase in the reaction temperature shortens the gelation time (Table-IV) probably on account of the easy availability of activation energy of gelation.

PROBABLE MECHANISM

The anodic polymerization of AA proceeds through free-radical species NO_3^\bullet , formed as stated earlier and /or HNO_3 generated in situ presumably according to the following reaction scheme.



The salt is decomposed at the anode, giving rise to active catalytic species stable in acidic solutions. NO_3^\bullet radical abstract hydrogen atom from the medium as suggested by Ross³ *et. al.* to produce HNO_3 which makes the solution acidic during electrolysis and may also catalyse the polymerization.

Indeed, we have observed⁴ that HNO_3 is quite capable of catalyzing the polymerization of AA, which is analogous to the anodic polymerization. In the presence of p-benzoquinone AA does not polymerize either

anodically or with HNO_3 indicating the possibility of a free radical polymerization. Nitrate radical or nitric acid may interact with AA to produce monomeric free radicals which give rise to polyacrylic acid with C-C chains.....

In summary the present work demonstrates that NaNO_3 acts as an initiator in electro-initiated polymerization of AA in H_2O medium. Further works on the quantitative aspects are in progress.

Table – I**Polymerization of AA at different current**

Current (mA)	Time of Electrolysis (min)	% conversion
10	240	Trace
20	240	6.00
40	240	8.00
60	240	10.00

Condition :

[AA] = 2.93 mole/l

[NaNO₃] = 1.180 x 10⁻³ mole/lTemperature, 40⁰C

Electrode, St. Steel – St. Steel

Table – III**Polymerization of AA of different concentration**

[AA] mole/l	Time of Electrolysis (min.)	% conversion
0.735	240	4.00
1.470	240	10.00
2.930	240	6.00
4.400	240	1.20

Condition :[NaNO₃] = 1.180 x 10⁻³ mole/l

Current = 40 mA

Electrode, St. Steel – St. Steel

Temperature, 40⁰C**Table – II****Polymerization of AA at different Electrolysis time**

Time of Electrolysis (min)	% conversion
60	Trace
120	2.5
240	8.7
480	13.90

Condition :

[AA] = 2.93 mole/l

[NaNO₃] = 1.180 x 10⁻³ mole/lTemperature, 40⁰C

Current = 40 mA

Electrode, St. Steel – St. Steel

Table – IV**Anodic Gel Polymerization of AA at different temperature**

Temperature ⁰ C	Time of Electrolysis (min.)	% conversion
25	240	25.0
40	240	10.0
60	240	8.00

Condition :

[AA] = 2.93 mole/l

Current = 40 mA

Electrode, St. Steel – St. Steel

[NaNO₃] = 1.180 x 10⁻³ mole/l

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